HALITE "THERMOMETER" FOR X-RAY INVESTIGATION OF SUBSTANCES IN THE TEMPERATURE INTERVAL FROM 77 TO 1037 °K

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ABSTRACT

A method is described in which a crystal or powder of halite (sodium chloride or common salt) serves as the standard determining the temperature of the substance being studied. The dependence of the glancing angle $\Theta^{\circ}_{(460)}$ of a NaCl crystal upon temperature is given for Cu-$K\alpha_1$- radiation.

This is close to a linear dependence in the 77 - 1037°K range. Employing a table or a graph showing the dependence of the angle $\Theta^{\circ}_{(460)}$ on temperature, one may readily determine the temperature of the substance being studied at the point where the X-rays pass through the samples and the standard at the angle $\Theta^{\circ}_{(460)}$ measured on a X-ray photograph.

In order to increase the accuracy with which X-ray photographs are evalu- /185
at,ed in an X-ray diffraction analysis, the method of a complex sample was recently employed – the simultaneous recording of the substance being studied and the standard (Ref. 1). NaCl is most frequently employed for this purpose when investigating Cu – $K\alpha_1$-radiation, namely, the intense reflection from the plane (460). A knowledge of the glancing angle $\Theta^{\circ}_{(460)}$ = 80°1.7' in the case 18°C (291 °K) provides great accuracy when measuring the effective radius of the cassette and the parameters of the elementary nucleus of the crystal being studied at room temperature (Ref. 1).

If a reflection with the index (460) is obtained on one and the same film at room temperature (291 °K) or at any other constant temperature T, °K, the value $\Theta^{T, \, °K}_{(460)}$ may be readily computed for the temperature T, °K according to the following formula

$$\Theta^{T \, °K}_{(460)} = \Theta^{291 \, °K}_{(460)} \pm \Delta\Theta^{0}_{(460)} .$$

At temperatures below 291 °K, $\Delta\Theta^{\circ}_{(460)}$ will have a plus sign, and correspondingly for temperatures above 291 °K, it will have a minus sign.

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*Numbers in the margin indicate pagination in the original foreign text.

Figure 1. X-ray Photograph of the Oscillation
of a NaCl Crystal. Reflections from the (460)
Plane in the Case T = 298° K, T = 463 °K and T =
523 °K. Angles Θ° for these Temperatures are
79°57', 77°54' and 77°12', respectively.

Thus obtaining the curve showing the dependence of the angle $\Theta^{\circ}_{(460)}$ on temperature for Cu – $K\alpha_1$-radiation, we may solve the opposite problem: measuring the angle $\Theta^{\circ}_{(460)}$ on an X-ray photograph, where the substance being studied which is covered by a NaCl powder is recorded, we must determine the temperature of the sample during the exposure time.

EXPERIMENTAL SECTION

In order to determine the glancing angle $\Theta^{\circ}_{(460)}$ at the temperature 77 °K, a roentgenometer is employed (Ref. 2) with a special Dewar flask with a valve. A thin stream of liquid nitrogen constantly cools the NaCl crystal during the recording. The X-ray photographs in the high temperature region were obtained on a RKV-86 camera. An electric micro-oven attached to a goniometric knob was employed to heat the crystal (Ref. 3).

The NaCl X-ray photograph, obtained at crystal temperatures of 298, 463 and 523 °K, is shown in Figure 1. For greater measurement accuracy, reflections /186 from the plane (460) from both sides of the primary beam were obtained. The farthest spots on the X-ray photograph ($K\alpha_1$ and $K\alpha_2$) correspond to a temperature of 298 °K. At a temperature of 463 °K, the reflections (460) $K\alpha_1$ shifted to the center of the film by 3.07 mm or 2°3'. At a temperature of 523 °K, the crystal slightly changed its alignment, and the spots lay barely below the 0-layer of the line. The angle Θ°_{460} for $K\alpha_1$ became smaller by 42' (shift of the spot $K\alpha_1$ by 1.05 mm).

For higher temperatures, this heating method cannot be employed, since the X-ray film overheats from thermal radiation. It was necessary to produce less powerful electric heating, but with a higher local temperature. For this purpose, a platinum wire of $\phi 0.2$ and a length of 30 mm was employed as the micro-oven. The platinum was heated by a current which was somewhat higher than the melting temperature of the crystal for a short period of time. After the wire has touched the crystal, the electric current is turned on and the crystal is firmly soldered

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to the platinum wire. X-ray photographs were obtained at temperatures of 708, 995 and 1037 °K. The power of the oven was so small that the temperature of the film and the cassette did not increase. The crystal temperature was measured by a platinum-gold palladium alloy (conductor, $\phi 0.1$ mm) microthermocouple, whose end was sealed into the crystal. The oscillation angle of the crystal 10 - 15° made it possible to employ this method when measuring the crystal temperature. Table 1 presents the values of the angle $\Theta^{\circ}_{(460)}$ at different temperatures.

TABLE 1

EXPERIMENTAL VALUES OF THE ANGLE $\Theta^{\circ}_{(460)}$, THE INTERPLANAR SPACING $d_{(460)}$, AND a AS A FUNCTION OF THE NaCl CRYSTAL TEMPERATURE.

$T°$, K	$\Theta_{(460)}$	d, Å	a, Å
77	82°40'±1'	0,77658 ±0,00003	5,6??? ±0,000?
298	79°57'±1'	0,78224 ±0,00004	5,6408 ±0,0003
321	79°39'±1'	0,78456 ±0,00004	5,6461 ±0,0003
372	78°02'±1'	0,78734 ±0,00005	5,6575 ±0,0004
423	78°25'±1'	0,78620 ±0,00005	5,6694 ±0,0004
463	77°54'±1'	0,78773 ±0,00005	5,6804 ±0,0004
523	77°12'±1'	0,78986 ±0,00005	5,6958 ±0,0004
708	75°06'±1'	0,79700 ±0,00006	5,7472 ±0,0004
995	72°00'±1'	0,80987 ±0,00008	5,8400 ±0,0006
1037	71°30'±1'	0,81221 ±0,00008	5,8569 ±0,0006

Based on the data given in Table 1, a curve was compiled showing the dependence of the glancing angle Θ° for the plane (460) of the NaCl crystal upon temperature (Fig. 2). Table 1 gives the measurement accuracy ±1 for the glancing angle $\Theta^{\circ}_{(460)}$. This accuracy was determined by measuring the distance on the X-ray photograph between the centers of the spots with the index (460) obtained at room temperature, and at any other constant temperature of the crystal. The case was chosen (the worst case for measurement accuracy) when the radius of the cassette R = 28.6 mm and of 1° of the angle Θ°, respectively, on the X-ray photograph corresponds to 1 mm. The measurement accuracy on the EZA-2 comparator fluctuated between ±0.017 mm or, when converted, by the angular amount ±1'.

The change in the angle $\Theta^{\circ}_{(460)}$ by 70' corresponds to a temperature change of 100 °K (Fig. 4). Consequently, a temperature change of 1.4° corresponds to one minute. Making a rough approximation of this value, we may assume that the temperature was measured with an accuracy of ±2°K in the 78 - 523 °K range, based on the X-ray photograph. It was difficult to make a precise analysis of the measurement errors for crystal temperatures above ∿600 °K. It may be stated that the crystal was at this temperature during the main portion of the exposure period, otherwise the spots on the X-ray photograph would have a form which was extended along the horizontal at a high temperature.

Based on the values of $\Theta^{\circ}_{(460)}$, the change in the interplanar spacing $d_{(460)}$ with temperature (temperature range of 50 °K) was determined from the graph, and the linear expansion coefficients of NaCl were computed (Table 2).

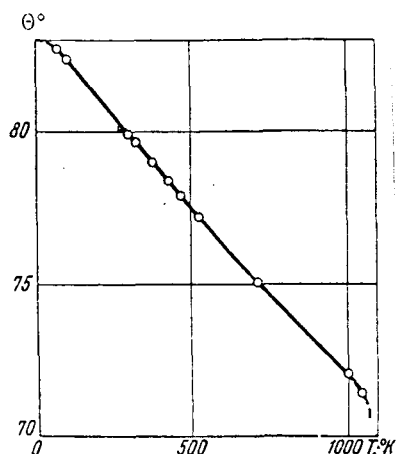In Table 2, the accuracy with which the angle $\Theta^{\circ}_{(460)}$ is determined is the

Figure 2. Dependence of the glancing Angle $\Theta^{\circ}_{(460)}$ on Temperature for Cu - $K\alpha_1$-Radiation.
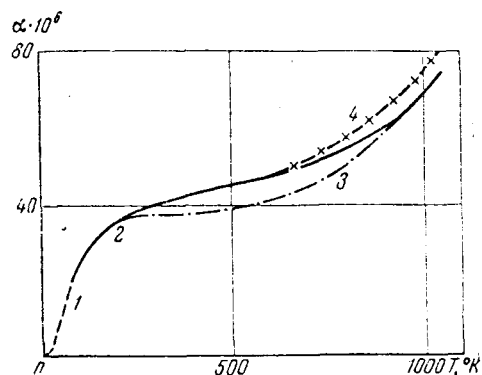

Figure 3. Dependence of the Linear Expansion Coefficient of Sodium Chloride on Temperature, Obtained by Different Measurement Methods. 1 - Interference Method 10 - 300 °K; 2 - X-Ray Method 77 - 1037 °K; 3 - Capacitance Dilatometer Method 300 - 1073 °K; 4 - Interference Method 300 - 1073 °K.

same as in Table 1. The values of the angles $\Theta^{\circ}_{(460)}$ in Table 2 are taken from the graph showing the dependence of the angle $\Theta^{\circ}_{(460)}$ on temperature (Figure 2). Measurements of the angle $\Theta^{\circ}_{(460)}$ with an accuracy of $\pm 1'$ at 82°42' provide an error of ± 0.00003 Å in the determination of the interplanar spacing $d_{(460)}$. With a decrease in the angle $\Theta^{\circ}_{(460)}$, the error in determining $d_{(460)}$ increased, and amounted to ± 0.00008 Å at 71°30'. This is indicated by the value of the linear expansion coefficient α, which was determined with an error of $\pm 2 . 10^{-6}$ at large angles $\Theta^{\circ}_{(460)}$ (low temperatures), and increased to $\pm 5 . 10^{-6}$ when there was a decrease in the angle $\Theta^{\circ}_{(460)}$ (high temperatures).

Figure 3 shows the curves for the expansion coefficient obtained by different methods. In the low-temperature region, the results derived from the study (curve 2) coincide, within the limits of experimental error, with the data obtained by the interference method (Ref. 4, 5) (curve 1 to 10 up to 300 °K). In the temperature region above room temperature, they coincide with data given in (Ref. 6), also obtained by the interference method. Curve 3 obtained on a capacitance dilatometer (Ref. 7) lies somewhat lower in the mean temperature region, and curve 4 (Ref. 8), on the other hand, lies somewhat above curve 2 in the high temperature region. The data given in (Ref. 7, 8) which are somewhat too low, or somewhat too high, may probably be explained by the difference in the samples, and by the inaccurate measurements. This is substantiated by the lack /188 of a divergence in the data in the low temperature region.

One advantage which the X-ray method has over the Fizeau method must be pointed out. The X-ray method makes it possible to employ small crystals, whereas it is necessary to have comparatively large crystals for the Fizeau

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TABLE 2

DEPENDENCE OF $\theta^\circ_{(460)}, d_{(460)}, a$ AND LINEAR EXPANSION COEFFICIENT α NaCl UPON TEMPERATURE.

| T, °K	$\theta^\circ_{(460)}$	$d_{(460)}$, Å	Δd, Å	T_{cp}, °K	$\alpha \cdot 10^6$
75	82°42′	0,77652			
125	82°10′	0,77749	0,00097	100	25±2
175	81°31′	0,77875	0,00126	150	32±2
225	80°52′	0,78013	0,00138	200	35±2
275	80°13,5′	0,78162	0,00149	250	38±2
325	79°35′	0,78318	0,00156	300	40±2
375	78°57′	0,78478	0,00160	350	41±3
425	78°21′	0,78644	0,00166	400	42±3
475	77°45′	0,78816	0,00172	450	43±3
525	77°11′	0,78993	0,00177	500	45±3
575	76°37′	0,79176	0,00183	550	46±3
625	76°03′	0,79365	0,00189	600	48±4
675	75°29′	0,79561	0,00196	650	49±4
725	74°56′	0,79764	0,00203	700	51±4
775	74°24′	0,79972	0,00208	750	52±4
825	73°51′	0,80187	0,00215	800	54±4
875	73°19′	0,80409	0,00222	850	56±5
925	72°46′	0,80645	0,00236	900	59±5
975	72°12′	0,80900	0,00255	950	63∓5
1025	71°36′	0,81175	0,00275	1000	68±5
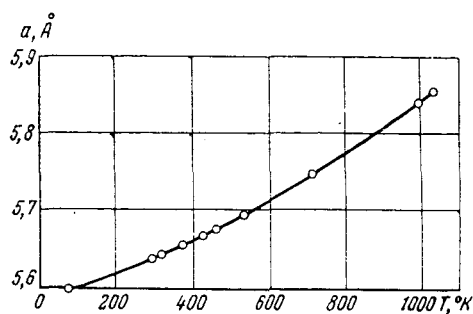
Figure 4. Change in the Lattice Parameter of a NaCl with Temperature.

method. In addition, the Fizeau method may be employed with great difficulty in the case of a non-cubic system of crystals, since oriented laminae must be cut out of a large crystal in a specific way in order to align the crystal in a certain crystallographic direction.

Based on experimental data, the pattern of the temperature curve for the lattice parameter a NaCl is shown in Figure 4.

The measurement of temperature based on the glancing angle $\theta^\circ_{(460)}$ was employed when determining the expansion tensor of crystals of naphthalene, anthracene, and 1,8-dinitronaphthalene. The following methods were employed when recording two different crystals on one film simultaneously: (1) the crystal being studied was dusted with a NaCl powder, resulting in the fact that there were Debye lines on the X-ray photograph from the NaCl powder.

The measurement was performed according to the (460) lines, corresponding to room temperature and to any other constant temperature; (2) when it was necessary to decrease the exposure and to obtain clear spots (460) at the same time, a crystal having the same dimension was attached from above to the NaCl crystal with a dimension of 1 x 1 x 1 mm³ with a high-temperature glue. The center of the X-ray bundle was heated at the boundary between the glued crystals. For purposes of verification, another experiment was performed. The NaCl was placed above the crystal to be studied. Under the same heating regime, no differences were detected in the values of the angle $\theta^\circ_{(460)}$ for the lower or upper position of the NaCl crystal.

Figure 5 shows an X-ray photograph of 1,8-dinitronaphthalene obtained at room temperature 297 and 343 °K. The crystal temperature 343 ± 2 °K was determined by measuring the distance between two given spots on the film. The found Δl, mm was recalculated in $\Delta\theta^\circ_{(460)}$ and the value of $\theta^\circ_{(460)}$ was determined. The

Figure 5. Roentgenometric Development, Obtained from Crystals of 1,8-Dinitronaphthalene and NaCl at Temperatures of 297 and 343 °K on one Film.

corresponding temperature, equalling 343 ± 2 °K, was determined from the curve showing the dependence of the angle $\Theta^{\circ}_{(460)}$ on temperature according to the determined angle $\Theta^{\circ}_{(460)}$.

In conclusion, I would like to express my appreciation to A. I. Kitaygorodskiy for his constant interest and attention to this study.

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